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Citation: [Applied Physics Letters](#) **86**, 123504 (2005); doi: 10.1063/1.1883321

View online: <http://dx.doi.org/10.1063/1.1883321>

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## Solid-state electrochromic devices based on poly (phenylene vinylene) polymers

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(Received 22 November 2004; accepted 24 January 2005; published online 15 March 2005)

We present a solid state electrochromic device based on poly (phenylene vinylene) light-emitting polymers and explore device performance as a function of salt type, salt concentration, and polymer layer thickness. Salts employing organic anions display improved optical contrasts. Higher salt concentrations and thicker devices produce higher optical contrasts at the cost of slower switching speeds. Devices display high reversibility, dramatic optical contrasts (>40%), and low operating voltages (<2 V) that are comparable to state-of-the-art conducting polymer electrochromic devices. © 2005 American Institute of Physics. [DOI: 10.1063/1.1883321]

Soluble light-emitting polymers based on poly (phenylene vinylene) (PPV) have been extensively studied for their use in applications such as light-emitting diodes<sup>1,2</sup> and photovoltaic cells;<sup>3,4</sup> however, understanding doping effects in these materials has largely been limited to light-emitting electrochemical cells.<sup>5,6</sup> This is surprising since doping can be used for controlling a wide variety of other interesting properties, including electrochromic<sup>7,8</sup> and piezoelectric effects.<sup>9</sup> In particular, the ability to control electrochromism in electroluminescent polymers opens up a wide range of potential technologies for integrated sensors and displays. In this letter, we report on the construction of a solid-state electrochromic device employing a PPV-based light-emitting polymer as the color-changing material. We show that the color changes observed for PPV-based materials have properties comparable to the best and most widely studied polymer electrochromic materials, such as polypyrrole and polythiophene.<sup>10-12</sup> By studying changes in the electrochromic properties as a function of dopant concentration and type and device thickness, we propose a model for understanding and optimizing the effect of doping on the transmission in PPV-based materials.

Solid-state electrochromic devices were constructed using the sandwich structure ITO/PPV polymer/gel-electrolyte/ITO. The polymer layer contained a blend of PPV-based polymer and poly(ethylene oxide) in chlorobenzene. For the PPV polymer, several materials were studied; for clarity, we focus our results on the most reproducible material, MEH-PPV {poly [2-methoxy-5-(2-ethylhexyloxy)-1,4-phenylenevinylene]}, although large band-gap materials resulted in more striking color changes.<sup>13</sup> The gel electrolyte consisted of salt, poly(methyl methacrylate), propylene carbonate, ethylene carbonate, and acetonitrile at 1:2.4:4:4.9, respectively. A variety of salt concentrations and types were tested, including Li triflate, tetrabutylammonium (TBA) triflate, TBA PF<sub>6</sub>, TBA BF<sub>4</sub>, and TBA p-toluene sulfonate. The devices were constructed by spin-casting the polymer solution to a thickness of 200 nm onto a glass/ITO substrate, annealing at 120 °C for 1 h, and drying in a vacuum chamber overnight. The gel electrolyte was then spin-cast onto a second ITO glass substrate, exposing to dry nitrogen for 20 min, and finally sandwiching with the other polymer/ITO sub-

strate to form the layered device. All device fabrication was performed in an inert atmosphere glove box to minimize exposure to water and oxygen.

The transmission spectra of the solid-state devices were taken with a Varian Cary 3 spectrophotometer in their pristine (nondoped) forms and then again after each device had been held at the given voltage for 2 min with a 2400 Keithley sourcemeter. The solution-based electrochemical experiments were performed using a nonaqueous silver/silver ion reference electrode, a platinum counter electrode and a MEH-PPV/ITO working electrode. Data were obtained on an EG&G Princeton Applied Research Model 362 Scanning potentiostat and two 2010 Keithley multimeters as the potential was scanned at 20 mV/s. Film thickness measurements ( $\pm 15$  nm) were taken using a Thermomicroscopes Autoprobe CP atomic force microscope. MEH-PPV was provided by American Dye Source and the ITO substrates were provided by Thin Film Devices, Inc.

In a polymer electrochromic device (ECD) operating in forward bias, the anions (namely triflate, PF<sub>6</sub>, BF<sub>4</sub>, and p-toluene sulfonate) diffuse into the polymer layer resulting in oxidation, or p-doping, of the polymer layer at the contact. For MEH-PPV, this results in a visible color change from orange-red to greenish-brown<sup>14</sup> beginning at approximately 1.5 V. The device may be operated in reverse bias resulting in reduction, or n-doping, of the polymer layer by the salt cation. The pristine and oxidized transmission spectra, device structure, and material structure for the MEH-PPV/gel electrolyte ECD are shown in Fig. 1. The color change is due to doping within the band gap of the polymer, as has been observed previously.<sup>15</sup> Optimal devices exhibited switching speeds of about 5 s, had large optical contrasts in the visible region (30%–50%) and were reversible during several days of testing. The performance of the devices thereafter depended heavily on their exposure to air. The devices with Li triflate and TBA triflate showed the highest optical contrast and were more reversible than those with TBA PF<sub>6</sub>, TBA BF<sub>4</sub>, or TBA p-toluene sulfonate at comparable concentrations. However, because Li triflate is highly hygroscopic, these devices were more susceptible to water contamination thereby shortening their lifetimes.

Experiments were performed in order to understand the dependence of the electrochromic material on polymer layer thickness, salt type, and salt concentration. Figure 2(a)

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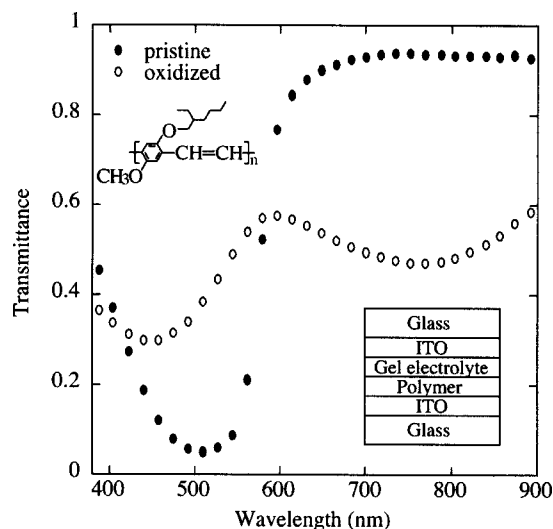


FIG. 1. ECD structure, MEH-PPV chemical structure, and the transmittance spectra for an undoped device (0 V) in comparison with that of a fully doped device (2 V). The salt is Li Triflate at a concentration of 1.8%.

demonstrates the dependence of the optical contrast ( $\Delta\%$ transmission) of our devices on the thickness of the polymer film. At low applied voltages, thicker devices exhibit a slight decrease in optical contrast; however, at higher voltages, the optical contrast increases with increasing film thickness. We interpret the thickness dependence as being due to the amount of the film that is doped for a given operating voltage. For low voltage, the film is only partially doped. Therefore in thicker films the lower field strength for the same operating voltage results in lower volume of doped material, and thus lower optical contrast. For higher voltage, however, the films are fully doped and thus the thicker films display higher optical contrast.

Figure 2(b) demonstrates the dependence of the optical contrast on the type of salt in the gel electrolyte. The data show that the optical contrast is approximately the same for Li triflate and TBA triflate and also for TBA  $\text{PF}_6$  and TBA  $\text{BF}_4$ . The optical contrast of the two triflates, however, is slightly higher than that of TBA  $\text{PF}_6$  and TBA  $\text{BF}_4$ . As expected, the oxidation of the polymer film does not depend on the cation of the salt. Differences in doping with salts with different anions, however, may be expected. The organic anions may be more effective at doping the polymer film than the inorganic salts, possibly due to greater solubility of the organic salt in the polymer matrix.

The dependence on salt concentration in electrolyte was examined with both solid-state devices and cyclic voltammetry. Figure 2(c) shows the dependence of the optical contrast of the solid-state devices on the salt concentration in the gel electrolyte for sufficient voltage application periods to achieve complete doping. At lower voltages, up to 1.4 V, the devices with lower salt concentrations have higher optical contrasts, but at applied voltages of 1.8 V and higher, the devices with a larger salt concentration have higher optical contrasts. Experiments performed with higher salt concentrations showed similar results with higher average optical contrasts but slower switching speeds. For a 5 s voltage application period, we observed a maximum in optical contrast of nearly 50% for Li triflate at a concentration of 8% and 2.4 V.

Figure 3 displays cyclic voltammograms for MEH-PPV films for a variety of electrolyte concentrations. As the con-

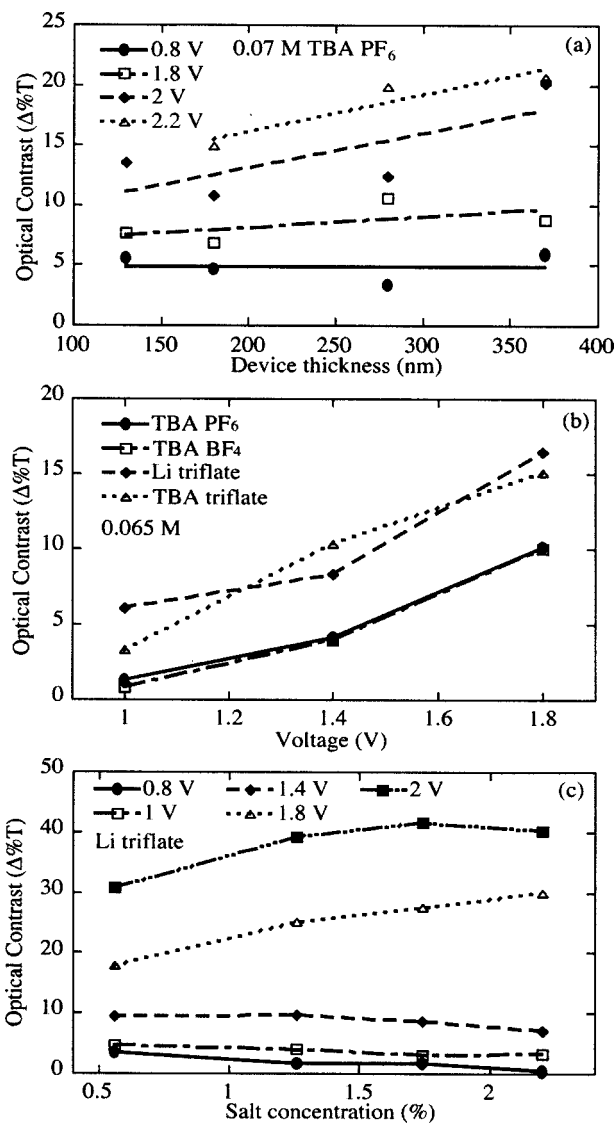


FIG. 2. Dependence of the optical contrast of a solid state device at 700 nm on (a) device thickness with a concentration of 0.07 M of TBA  $\text{PF}_6$ ; (b) salt type each at 0.65 M; and (c) salt concentration measure in weight percentage of Li triflate.

centration of salt is increased from 2.5 to 10 mM, the anodic peak moves to lower voltages. As the salt concentration is further increased from 10 to 40 mM, the anodic peak shifts back to higher voltages. These results can be interpreted as being due to the dependence of the conductivity of the electrolyte on salt concentration. Previous results have observed a maximum in the conductivity of salt electrolytes occurring with salt concentration.<sup>16,17</sup> Increasing the number of ions past this optimal concentration lowers the conductivity because of a rise in the viscosity of the solution due to ion pairing and other electrodynamic effects. In the cyclic voltammetry results, increasing the salt concentration up to 10 mM increases the rate of doping reaction indicating that more ions are present in the material. Past a 10 mM concentration, the reaction is slowed due to a decrease in ion mobility, and aggregation of ions in the electrolyte affects the doping of the material. Similarly, in the solid state devices, lower voltages are less able to break apart or move the aggregates naturally present in the electrolyte that increase with increasing concentration, thus we observe a decrease in the optical contrast. For higher salt concentrations and higher

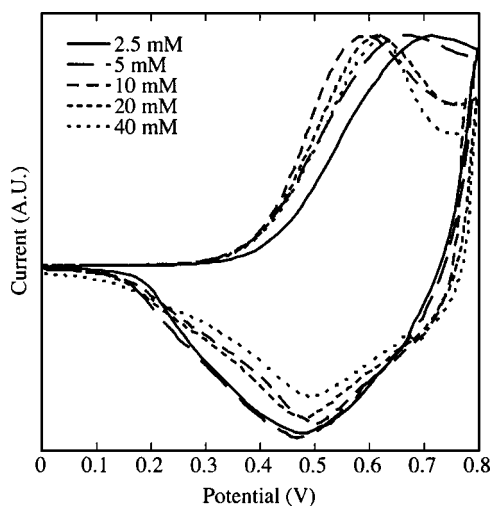


FIG. 3. Cyclic voltammograms normalized at the anodic peak taken at 20 mV/s for varying salt concentrations from 2.5 to 40 mM.

voltages, the optical contrast depends largely on the doping time intervals. Therefore, when the voltage application period is small, we observe a peak in the optical contrast indicating an optimal salt concentration.

In conclusion, an ECD was constructed from light-emitting polymer MEH-PPV that exhibited visible change in color and reversible characteristics. The degree of the voltage-dependent color change is dependent on polymer layer thickness, anion type, and salt concentration. Visible color change begins at about 1.5 V, but a voltage of about 1.8 V is necessary to fully dope the polymer film. Preliminary results suggest that organic anions result in higher optical contrasts and that the limiting factor in the dependence of optical contrast on salt concentration is related to the time interval in which the doping reaction is allowed to take

place. These results have implications for controlling doping in PPV-based polymer LECs, actuators, and sensors.

The authors gratefully acknowledge support from NSF ECS Grant No. 0101794.

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